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The rates of dissociation of 2 : 2′-azo-*bis*-*iso*butyronitrile (AZBN) and pentaphenylethane (PPE) have been measured in toluene at pressures up to 10,000 and 1500 atm respectively and were found to be decreased by hydrostatic pressure. The effect is as predicted by considering only the volume change due to a 10 % extension of the reacting bond in forming the activated state, although when using iodine as a scavenger with AZBN one finds a much larger pressure effect, presumably due to changes in the " cage effect ". The pressure effect on the dissociation equilibrium of nitrogen tetroxide in carbon tetrachloride solution has been measured at pressures up to 1500 atm and was found to be ten times as great as predicted from the changes in molecular volumes.

The effect of pressure on the rates of ionic reactions can largely be explained in terms of the changes in the energy of solvation brought about by pressure.[1, 2, 3, 4] The rates of free-radical dissociations are known to be little influenced by the nature of the reaction medium and it is therefore unlikely that solvation energies are major factors in the energy changes of such reactions. One would thus expect the effect of pressure on these reactions to be much smaller than for ionic reactions.

In the present investigation the effect of pressure on three free-radical dissociations has been observed. The rate of dissociation of 2 : 2′-azo-*bis*-*iso*butyronitrile (AZBN) in toluene has been measured in two ways; the disappearance of AZBN was followed directly by observing the light absorption at three characteristic wavelengths,[5] and the formation of free radicals was observed indirectly by using iodine as a scavenger and following its disappearance on a spectrophotometer.[6] By the direct method, measurements were made at 1 and 1500 atm at 70° C, while the scavenger method was used to follow the reaction up to 10,000 atm at 62·5° C.

The use of iodine in measuring the dissociation of AZBN has been investigated in some detail by Hammond *et al.*[6] who found the efficiency of the scavenging reaction to vary in different solvents. It is known that the " cage effect " is very pronounced in this dissociation due to the possibility that the two primary free-radical fragments react to eliminate nitrogen and form the stable tetramethylsuccinodinitrile before they diffuse apart (Hamill *et al.*).[7]

This effect is specific to AZBN and should not apply to the dissociation of pentaphenylethane (PPE) which was investigated as the second substance. The use of iodine to measure the rate of this type of dissociation was first introduced by Ziegler, Ewald and Orth [8] and was widely used by Bachmann.[9] Since the formation of triphenylmethyl iodide in this reaction with iodine is reversible these workers found it necessary to introduce pyridine and ethanol to react further with the iodide. In the present investigation the need for this was avoided by using a large excess of PPE and following only the first few percent of the dissociation, in the manner of Bawn and Mellish.[10] The dissociation of PPE was measured in toluene at 70° C and at pressures up to 1500 atm.

The third system investigated was the equilibrium between nitrogen tetroxide and nitrogen dioxide in carbon tetrachloride solution. This equilibrium was measured at 22° and 51·5° C and at pressures up to 1500 atm.

EXPERIMENTAL

All the reactions were followed by means of a Unicam S.P. 500 spectrophotometer which was modified to accommodate a high-pressure absorption cell.[11] At pressures up to 1700 atm (up to 3000 atm in one case) the reactions were carried out directly in this cell and could be observed continuously. For reactions above 3000 atm the reaction mixture was enclosed in either an all-glass or an all-Teflon reaction tube having at one end a well-fitting plug which could slide into the tube to transmit pressure to the reaction mixture. These cells were immersed in oil in a steel bomb of 1-in. int. diam., of the type described by David and Hamann.[2] At the end of a run the reaction cell was removed from the bomb, chilled, and the contents were then analysed in an ordinary stoppered spectrophotometer cell.

2 : 2′-AZO-*bis-iso*BUTYRONITRILE

This was prepared by the method of Thiele and Heuser [12] and the final product melted at 104-105° C. A.R. toluene was carefully purified by the usual methods and finally fractionally distilled from sodium and stored over sodium. The solutions for the direct measurements were made up by weighing and were approximately 0·6 M. The rate constants were calculated from the observed optical densities D at 350, 370, 280 mμ [4] by the equation

$$k = -(1/t)\ln(D/D_0). \qquad (1)$$

The method of least squares was used to find the best value of k for any one plot of D against time t. The results are quoted in table 1 and are the means of the values found at the three wavelengths.

The reactions using iodine as a scavenger were carried out in the manner of Bawn and Mellish [10] using a 20- to 50-fold excess of AZBN over iodine. The solutions of AZBN in toluene were made up by weight and were freed of oxygen by bubbling purified nitrogen saturated with toluene through them. These solutions were then mixed with similarly deoxygenated solutions of iodine so that the reaction mixtures were approximately 0·001 m in iodine and 0·057 m in AZBN, except in a few cases when half this concentration of AZBN was used in order to check the first-order character of the reaction.

The reaction was followed by measuring the iodine absorption at 500 mμ at short intervals. In order to eliminate any optical effects due to the pressure applied to the cell the optical density was also measured at 950 mμ since the reaction mixture was known to be quite transparent at this wavelength. These measurements were used as a correction to the readings at 500 mμ.* A plot of D against time gave straight lines and the reaction rates were calculated from the slope by the equation

$$k = -\frac{1}{\epsilon' l}\,\frac{\mathrm{d}D}{\mathrm{d}t}\,\frac{1}{[\mathrm{AZBN}]_0}. \qquad (2)$$

Here ϵ' is the molal extinction coefficient of iodine at the temperature and pressure of the particular experiment, l is the optical path length of the absorption cell, and concentrations are expressed in mole/kg. Values of ϵ' were determined in separate experiments using analysed solutions of iodine in toluene.

TABLE 1.—DISSOCIATION OF 2 : 2′-AZO-*bis-iso*BUTYRONITRILE IN TOLUENE

presssure atm	$k \times 10^5$ (sec^{-1}) 70° C direct	$k \times 10^5$ (sec^{-1}) 62·5° C direct	$k \times 10^5$ (sec^{-1}) 62·5° C scavenger	$\frac{k\text{ (scavenger)}}{k\text{ (direct)}}$
1	5·50	1·87	0·892	0·447
1500	4·47	1·52	0·552	0·363

Some rate constants obtained by the two methods are shown in table 1. The third column of the table gives the rate constant at 62·5° C calculated from the direct measurements at 70° C by using the energy of activation $\Delta E^{\ddagger} = 31 \cdot 1$ kcal/mole found by Talât-Erben and Bywater [5] and confirmed in the present investigation. Further results obtained by the scavenger method are shown in fig. 1. The upper of the two rate constant curves shows the results of a run in which particular care was taken to exclude all oxygen by handling the solutions only in an atmosphere of carbon dioxide. The higher rate constants obtained in this run show the inhibiting effect of oxygen on the scavenging reaction between iodine and the free radicals, although there was no actual induction period as was found in the PPE system. The top curve on fig. 1 shows values of $\log_{10}(k_p/k_1)$ calculated for individual runs. The close agreement in this ratio between different runs shows that it is not affected by the presence of a trace of oxygen.

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* This method of correction was used with all the spectrophotometer measurements.

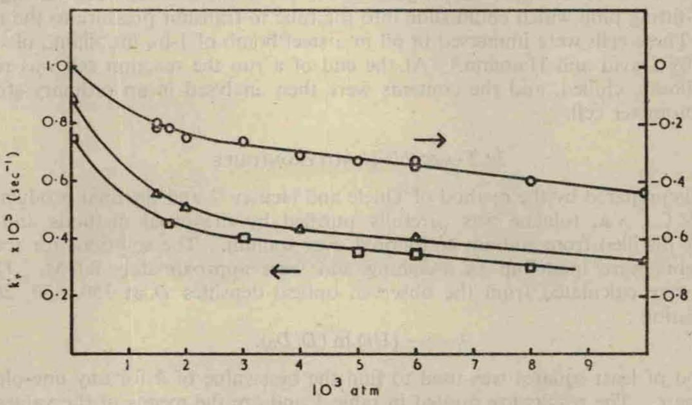

FIG. 1.—The dissociation of AZBN in toluene at 62·5° C.

PENTAPHENYLETHANE

This substance was prepared by coupling diphenylmethyl chloride with triphenylmethyl sodium in the manner of Bachmann and Wiselogle.[13] The final product melted with decomposition between 168 and 172° C.

The reaction with iodine was carried out in the same manner as for AZBN using solutions 0·001 m in iodine and between 0·015 and 0·025 m in PPE. The reaction, however, seemed to be more sensitive to the presence of oxygen. Although nitrogen was bubbled through the solutions and these were handled afterwards only in an atmosphere of carbon dioxide, the plots of optical density against time showed an induction period during which iodine disappeared at a slower rate than during the remainder of the reaction. This induction period usually lasted for only a small part of the time during which the reaction was followed. Fig. 2 shows the reaction curves obtained in one series of runs.

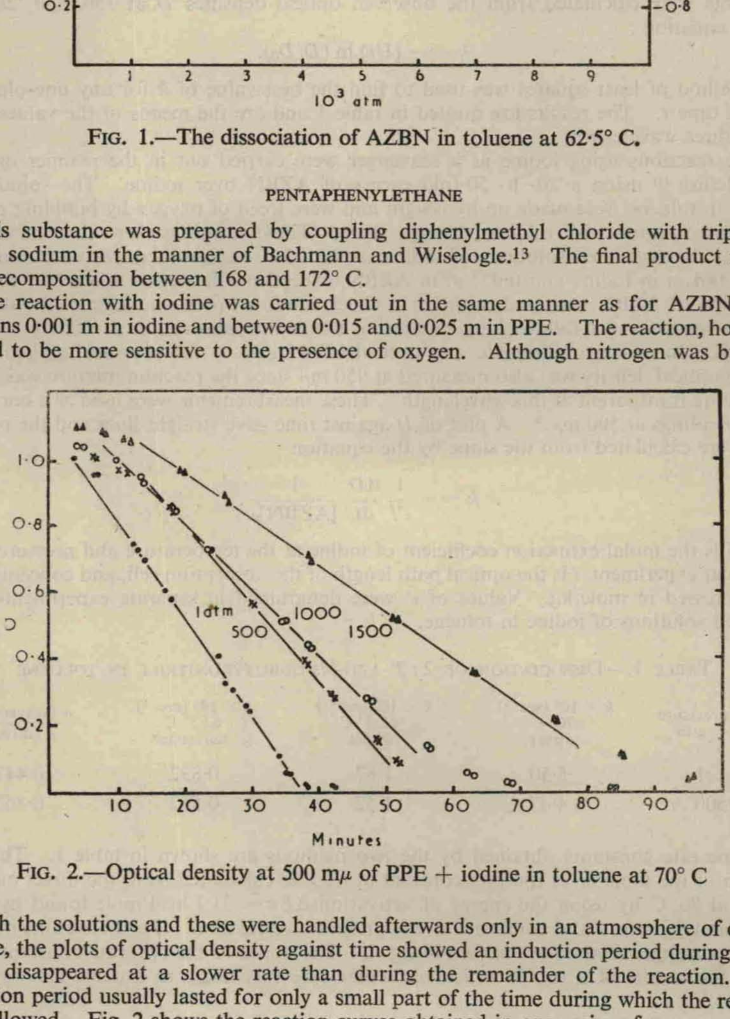

FIG. 2.—Optical density at 500 mμ of PPE + iodine in toluene at 70° C

The rate of dissociation of PPE at 70° C was calculated from the slope of the linear portion of a plot of the optical density at 500 mμ against time, by using eqn. (2). The mean of the rate constants found at 1 atm was $2{\cdot}5 \pm 0{\cdot}25 \times 10^{-5}$ sec^{-1} which is rather lower than the value found by Bachmann [9] in xylene ($5{\cdot}8 \times 10^{-5}$ sec^{-1}). Although the spread of the rate constants found in different runs was rather great the ratios k_p/k_1 calculated from different runs were in much better agreement. These ratios are shown in fig. 3.

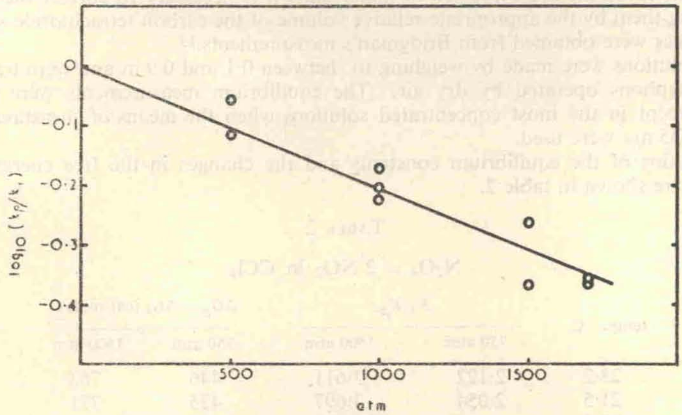

FIG. 3.—The dissociation of PPE in toluene at 70° C.

NITROGEN TETROXIDE

Nitrogen tetroxide was prepared by heating dried lead nitrate to 450° C in a current of dry oxygen. The gas was passed through two U-tubes packed with Raschig rings and phosphorus pentoxide and was condensed in a tube cooled in an ice + salt mixture. It was once more distilled through phosphorus pentoxide before use.

The carbon tetrachloride used to make the solutions had to be very pure and absolutely dry in order to obtain reasonably stable solutions. A.R. carbon tetrachloride was therefore fractionally distilled immediately before use and was exposed to air and light as little as possible.

The dissociation constant of nitrogen tetroxide is given by

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{2\alpha^2 m_0}{1 - \alpha}, \tag{3}$$

where α is the degree of dissociation and m_0 the total concentration of nitrogen oxides expressed as moles NO_2/kg. Nitrogen dioxide in CCl_4 has a strong absorption band with a maximum at 435 mμ and a pronounced shoulder at 550-555 mμ, while nitrogen tetroxide is quite transparent in this spectral region. Unfortunately it was not possible to find the molecular absorption coefficient of nitrogen dioxide because of the instability of the very dilute solutions required in order to extrapolate to zero concentration and complete dissociation. The dissociation constant of $12{\cdot}35 \times 10^{-4}$ (molal) found by Attwood and Roleffson [14] at 25° C, however, shows that α becomes very small in approximately 0·1 m solutions. If, then, $\alpha \ll 1$ we can write (3) as

$$K = 2\alpha^2 m_0, \tag{3'}$$

and the optical density of the solution is given by

$$D = \epsilon_{NO_2} l \alpha m_0 . \tag{4}$$

Combining these two equations we find

$$D \propto m_0^{\frac{1}{2}}, \tag{5}$$

and this relation was found to apply within the range of 0·3 to 1·0 m solution which was used in the equilibrium measurements.

From eqn. (3′) and (4) we also find that

$$K_1/K_p = D_1{}^2/D_p{}^2 \tag{6}$$

and the change of the free energy of dissociation with pressure is then given by

$$\Delta G_p - \Delta G_1 = RT \ln (K_1/K_p) = RT \ln (D_1{}^2/D_p{}^2(. \tag{7}$$

Since the optical densities are proportional to the volume concentration while the equilibrium constants are expressed in molal units it is necessary to correct the densities by dividing them by the appropriate relative volume of the carbon tetrachloride solutions. These values were obtained from Bridgman's measurements.[15]

The solutions were made by weighing to between 0·1 and 0·9 m and were transferred through syphons operated by dry air. The equilibrium measurements were made at 435 mμ except in the most concentrated solutions when the means of measurements at 550 and 555 mμ were used.

The ratios of the equilibrium constants and the changes in the free energy of dissociation are shown in table 2.

TABLE 2

$N_2O_4 \rightleftharpoons 2\,NO_2$ in CCl_4

temp. ° C	K_1/K_p		$\Delta G_p - \Delta G_1$ (cal/mole)	
	750 atm	1500 atm	750 atm	1500 atm
23·2	2·122	3·611	446	763
21·5	2·054	3·697	425	771
22·5		4·025		825
23·1		3·775		788
mean 22	2·08	3·77	435	787
51	2·48	4·35	588	953
52	2·13	3·77	421	863
mean 51·5	2·30	4·06	540	908

DISCUSSION

Although it has been shown that the Stearn-Eyring [16] theory does not correctly describe the effect of pressure on ionic reactions [1] it could be expected to apply more nearly to the homolytic bond fissions occurring in free-radical dissociations.

In the dissociation of AZBN the first bond broken is a C—N bond.[5] If we assume a 10 % stretching of this bond and a constant cross-section of the molecule in passing from the initial to the activated state, we can calculate from a crude molecular model, using covalent radii for the bond lengths and van der Waals radii for the atoms, that the volume of activation should be $\Delta V^{\ddagger} = 4{\cdot}3$ cm^3/mole. From the equation

$$\frac{\mathrm{d} \ln k}{\mathrm{d}p} = -\frac{\Delta V^{\ddagger}}{RT} \tag{8}$$

and from the values of the rate constants shown in table 1 we find from the direct measurements $\Delta V^{\ddagger} = 3{\cdot}8$ cm^3/mole and from the scavenger measurements $\Delta V^{\ddagger} = 9{\cdot}36$ cm^3/mole.

If we make a similar rough calculation of the volume of activation of the dissociation of PPE we find a value of $\Delta V^{\ddagger} = 10{\cdot}5$ cm^3/mole, while the measured values of the rate of dissociation at 1 and 1000 atm give a value of $\Delta V^{\ddagger} = 13{\cdot}1$ cm^3/mole.

It is thus apparent that even in this crude form the assumption that the effect of pressure is purely a volume effect and that in the activated state there is a 10 % extension of the reacting bond gives the right sort of answer for these reactions.

The much larger effect of pressure on the rate of dissociation of AZBN found by the iodine scavenger method must be attributed to changes in the " cage effect " due to pressure. The ratio of these rates to the rates found by the direct method (which are independent of the fate of the free radicals after dissociation) are shown in table 1 and are an indication of the efficiency of AZBN as a source of available free radicals.

A much more stringent test of the assumption that the effect of pressure on free-radical dissociations is solely due to the volume changes involved in breaking a bond, should be provided by the measurements of the dissociation constant of nitrogen tetroxide. Not only should the result of the calculation here be independent of any assumptions regarding the activated state, but there are also much more accurate data available on which to base a theoretical calculation of the volume change.

By using X-ray diffraction data on N_2O_4 [17] and electron diffraction data on NO_2 [18] for the bond lengths and van der Waals radii for the atoms one finds that there is a volume increase of 2·1 cm^3 when one mole of nitrogen tetroxide dissociates. From the data of table 2 one can on the other hand derive that the pressure effect on the dissociation constant is equivalent to a volume increase of about 23 cm^3/mole. In this case therefore the assumptions made about the effect of pressure on the dissociation are quite inadequate. It is concluded that there is some interaction between the solvent and the nitrogen oxides which is changed by the application of pressure.

The retardation of free-radical dissociations by pressure found in these experiments is of the kind one would expect from general considerations but which so far has never been demonstrated experimentally. Merrett and Norrish [19] refer to some measurements of the rate of dissociation of benzoyl peroxide under pressure, but these appear never to have been published.

It follows from the present results that the large acceleration of polymerization reactions by pressure, which has been observed,[19] is not due to an increase in the rate of initiation but must be due to some other step in the polymerization.

It is a pleasure to acknowledge the help and stimulus derived from many discussions with Dr. S. D. Hamann and the help of Mr. H. G. David in running the high-pressure equipment.

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[1] Buchanan and Hamann, *Trans. Faraday Soc.*, 1953, **49,** 1425.
[2] David and Hamann, *Trans. Faraday Soc.*, 1954, **50,** 1188.
[3] Hamann and Strauss, *Trans. Faraday Soc.*, 1955, **51,** 1684.
[4] Burris and Laidler, *Trans. Faraday Soc.*, 1955, **51,** 1497.
[5] Talât-Erben and Bywater, *J. Amer. Chem. Soc.*, 1955, **77,** 3710, 3712.
[6] Hammond, Sen and Boozer, *J. Amer. Chem. Soc.*, 1955, **77,** 3244.
[7] Roy, Nash, Williams and Hamill, *J. Amer. Chem. Soc.*, 1956, **78,** 519.
[8] Ziegler, Ewald and Orth, *Annalen*, 1930, **479,** 277.
[9] Bachmann and Osborn, *J. Org. Chem.*, 1940, **5,** 29.
[10] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47,** 1216.
[11] Ewald and Hamann, *Austral. J. Chem.*, 1956, **9,** 54.
[12] Thiele and Heuser, *Annalen*, 1896, **290,** 1.
[13] Bachmann and Wiselogle, *J. Org. Chem.*, 1936, **1,** 354.
[14] Attwood and Roleffson, *J. Chem. Physics*, 1941, **9,** 506.
[15] Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1930, **66,** 213.
[16] Glasstone, Laidler and Eyring, *Theory of Rate Processes* (McGraw-Hill, New York, 1941), p. 470.
[17] Broadley and Robertson, *Nature*, 1949, **164,** 915.
[18] Maxwell and Mosley, *J. Chem. Physics*, 1940, **8,** 738.
[19] Merrett and Norrish, *Proc. Roy. Soc. A*, 1951, **206,** 309.

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